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(54) Abrasive articles.

(57) Abrasive articles especially tools are described which comprise abrasive grits held in a glass-ceramic bond in which at least 75% of the bond material is in bond posts or in coatings on individual grains.

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Background of the Invention

This invention relates to abrasive articles

A vitreous bonded abrasive product, such as a conventional grinding wheel, comprises three volume components: an abrasive particulate material which usually occupies about 40 to 50 vol%; a vitreous bond material that provides typically about 5 to 15 vol% of the total; and the balance of the volume is void space. The function of the bond material is to hold the abrasive particles in place so that they can do the abrading work. In a typical vitreous bonded product of the prior art the glass components are added to the abrasive particles and the mixture is heated till the glass components melt, fuse to form a glass, and then flow to the particle contact points to form a bond post that solidifies on cooling. This provides the rigid structure of the finished product. In a more recent method the glass bond material is formed separately as a molten mass, cooled to solidify and then ground up. This ground up material, known as a frit, is then mixed with the abrasive particles. The advantage of this procedure is that the heating step can be shortened, the bond composition is more uniform and the forming temperature can often be reduced.

It will be appreciated that the rigidity and strength of the products of the prior art are often determined by the bond posts. Glass, being an amorphous material, has a low strength, (about 40 to about 70 MPa), by comparison with the abrasive particles. This low strength gives rise to premature release of grain and enhanced wear. Hence the grinding ability of vitreous bonded products is in theory limited by the strength of the posts. In practice, with most abrasives, such limitations were not very significant. Some more modern abrasives however are adapted to perform best under a heavy load and this puts the bond under considerable stress. Traditional glass bonds are often found inadequate under such conditions and there is therefore a need for vitreous-based bonds with a greater ability to operate under high stresses.

It has been proposed that there might be advantage in the use of a glass-ceramic bond to bond abrasives. However it has not been found possible heretofore to ensure that the bond material is concentrated in the bond posts or in coating the abrasive grits. This of course is extremely inefficient and has not resulted in any commercialization of such glass-ceramic bonded materials in spite of the potential advantages that might be expected.

The present invention provides such a bond material. It has significantly greater strength than traditional bonds and is easily formed. Abrasive products comprising such bond materials often perform substantially better than those made with prior art bonds. The bonds can be used with a wide variety of abrasives and exhibit an impressive versatility in the kinds of abrasive products that can be made with them.

The present invention also provides a bonded abrasive product or article according to independent claim 1. Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description and examples.

The invention provides bonded abrasive articles and particularly those bonded with a bond material that can be converted to a semi-crystalline ceramic bond.

The abrasive products or articles of the invention preferably comprise abrasive particles held together by a glass-ceramic bond material wherein at least 75% of the bond material is present in the form of bond posts or a coating on the abrasive particles.

Glass-ceramic materials are defined for the purposes of this specification as materials that are processed and formed as glasses but which, on heating, can be converted to a semi-crystalline material with a crystallinity of at least about 50% and more preferably exceeding 80%, and a grain size, (longest dimension), of less than about 10  $\mu\text{m}$  and preferably of about a micron or even less.

The glass ceramic can be tailored to the abrasive particle with which it is to be used so that it has a matched coefficient of thermal expansion, for example within 20% of that of the abrasive. This may often result in reduced thermal stresses within the structure and consequently enhanced strength. While such a match of expansion coefficients may often be desirable, it is not an essential feature of the broadest aspect of the present invention. The degree of crystallinity can be adjusted to give a match of the mechanical strength of the bond with the abrasive particles or to ensure that the particles release when they have been smoothed and cease to cut effectively.

The use of glass-ceramic bonds in a vitreous bonded abrasive wheel enables the wheel to be operated at higher rotational speeds because of the greater mechanical strength of the wheel. In addition it permits the use of less bond material to achieve a comparable level of performance as can be obtained with conventional vitreous bond materials. The greater bond strength also results in better corner holding and overall a significantly improved wheel by comparison with the prior art wheels made with conventional vitreous bonds.

The physical mechanism by which these results are obtained is not completely understood but it is thought to be related to the fracture mechanism in glasses. In an amorphous structure crack propagation is

uninhibited by intervening structures and so the crack propagates until it reaches a surface and the glass breaks. In a glass-ceramic however the microcrystals dispersed in the glass matrix appear to cause crack branching which limits propagation and thus maintains the integrity of the structure far longer.

Glass-ceramic compositions tend to nucleate and crystallize at high viscosities and this tends to arrest deformation and densification. The selection of the components is therefore a matter of great importance. The key parameters are that the glass must flow, wet the abrasive particles, and form dense bond posts before, or at least concurrent with, the onset of crystallization. The flow properties are particularly important so as to ensure that the bond material in the final product is located in the bond posts or in a coating on the abrasive grits rather than in separated non-functional areas of the bonded material. In the present invention at least about 75% and preferably at least about 85%, or higher, is present in these locations, indicating that the desired degree of flow and coating has been achieved.

In the production of a glass-ceramic bonded abrasive article, the components are melted into a glass which is then cooled and ground to a powder, preferably one with a particle size of about 200 mesh\* or finer. In general, the finer the powder the better. This is because the surfaces of the particles present a plurality of potential surface nucleation sites and the greater the surface area of the glass powder, the larger the number of sites at which the desirable crystallinity can be initiated. The glass powder is then mixed with the abrasive in the requisite proportions along with any temporary binders, plasticizers and the like that may be desired. This mixture is then formed into a bonded abrasive product using conventional equipment. The critical parameter that determines the degree of crystallinity, (apart from the composition), is the firing schedule. This varies with the composition of the glass-ceramic and controls not only the degree of crystallinity but also the size of the crystals and ultimately the properties of the glass-ceramic. The firing schedule is often, but not essentially, a multi-step operation. In a typical schedule the dense glass bond posts are formed at an optimal temperature that is determined by the glass components. The product is then brought to the optimal nucleation temperature, (usually from about 30° C below, to about 150° C above the annealing temperature), for a fixed time, followed by a period at the optimal crystal growth temperature. As an alternative, with certain glass formulations, it is possible to carry out simultaneous 200 mesh = 74  $\mu$ m.

nucleation and crystal growth at the bond post formation temperature.

This procedure gives rise to dense glass-ceramic bond posts that have significantly greater strengths than those of conventional glass bonds.

In some cases it is possible to provide that the crystalline material separating from the glass melt is itself an abrasive and contributes to the abrasive properties of the final product. In an extreme situation this separating abrasive material is the sole abrasive component of the mixture such that the abrasive is, so to speak, generated "in situ". In such an event however the desirable porosity of the abrasive composite must be supplied by other means such as sacrificial components, blowing agents or the like.

The invention is now described with reference to certain preferred embodiments which are presented to provide illustrations of the invention

Figure 1 presents two SEM micrographs at magnifications of 150, (1a), and 900, (1b), of a bonded structure according to the invention. Figure 1a shows the abrasive particles with the bond in place; Figure 1b shows a single bond post and its microstructure. As can be seen the bond post comprises a plurality of fibrous crystals with random orientation. There is also a small amount of residual porosity.

Figure 2 comprises two SEM micrographs illustrating other kinds of crystal structure that can be present in a glass ceramic. Figure 2a shows spheroidal, and 2b shows dendritic crystal structures. Such structures can be obtained by suitable modifications to the firing schedules and the proportions of the components included in the mixture from which the glass-ceramic is formed.

Figure 3 shows graphs comparing the properties of bonded wheels that are identical except in terms of the bond. A conventional vitreous bond is compared with a glass-ceramic bond in accordance with the invention. The properties compared are G-Ratio and Cutting ability. The wheel according to the invention is the same as that described above in Figure 1. The comparative wheel uses a commercial vitreous bond.

The production of a bonded product according to the invention is further illustrated with reference to the following Example.

#### Example 1

A glass-ceramic bond material was made by preparing a lithium aluminosilicate, (LAS), glass powder having the composition shown in Table 1 below. The glass was obtained from Sandia National Laboratories under the designation "SB Glass". The composition information included below was derived from that

source.

Table 1

Raw Composition (wt%)		Fused Composition (wt%)	
SiO <sub>2</sub>	61.2	SiO <sub>2</sub>	74.4
Al <sub>2</sub> O <sub>3</sub>	4.1	Al <sub>2</sub> O <sub>3</sub>	5.0
H <sub>3</sub> BO <sub>3</sub>	1.9	B <sub>2</sub> O <sub>3</sub>	1.3
Li <sub>2</sub> CO <sub>3</sub>	25.6	Li <sub>2</sub> O	12.5
K <sub>2</sub> CO <sub>3</sub>	5.1	K <sub>2</sub> O	4.2
P <sub>2</sub> O <sub>5</sub>	2.1	P <sub>2</sub> O <sub>5</sub>	2.6

The glass batch was melted at about 1400-1500 °C in a platinum crucible. The melting time was about 24 hours. The melting glass was intermittently stirred. Glass granules were prepared by water quenching the molten glass and then comminuting, (using a ball mill), to about 200 mesh or smaller by ball milling with alumina balls in an alumina mill for about 15 hours.

The glass powder was mixed with abrasive grains of an alpha-alumina, (SG Alumina), prepared by a seeded sol gel process, (microcrystalline size of about 0.2 µm), as described in USP 4,623,364 and a temporary binder in the proportions shown in Table 2. The mixture was then subjected to the firing schedule which is also set forth in Table 2, as it was formed into a grinding wheel.

Table 2

Mix formula (wt%)	
SG (80 grit)	87.94
Citric Acid (50% soln.)	2.02
Dextrin (first addition)	0.88
Dextrin (secon addition)	0.94
Glass frit	8.21
(The Dextrin was derived from corn starch.)	

#### Firing Schedule

Ramp: Room Temp. to 640 °C at 150 °C/hour  
 Soak: One hour  
 Ramp: 640 °C to 930 °C at 25 °C/minute  
 Soak: One Hour

At the same time a wheel was made from the same abrasive grain using a commercial vitreous bond used by Norton Co. in the production of vitreous bonded wheels. The bond is identified as HA4C. The same amount of bond and abrasive was used to produce a wheel of the same grade as the wheel of the invention whose production is described above.

Typical SEM micrographs of the wheel of the invention are shown in Figure 1. Figure 1a shows that the bond has good flow and wetting of the grain particles and that good bond geometry has been achieved. The micrograph shows clearly that essentially all the bond material is located in bond posts or in a coating of the grain surface. Figure 1b shows that the bond comprises predominantly of needle-like crystals dispersed in a glassy phase. The needles are determined, by X-Ray Diffraction techniques, to be lithium silicate with the formula Li<sub>2</sub>SiO<sub>3</sub>. In addition lithium phosphate and cristobalite crystals are present, as determined by X-ray diffraction, and the overall crystallinity in the bond was determined to be about 50%. This product as indicated below showed adequate performance but it is anticipated that a higher overall crystallinity will yield even better results.

The performance of the glass ceramic bonded wheel was compared with the wheel having the HA4C bond and the results are set forth in Table 3. The test consisted of the external wet grinding of hardened 52100 bearing steel, (Rc 58) using a 5% aqueous solution of Trim VHPE 300 fluid. The wheel speed was 12400 rpm and the workspeed was 100 rpm. The volume of metal removed per unit volume of wheel wear,

(S/W or "the G-Ratio), was measured. This determines in practice the total amount of metal that can be removed before the wheel has to be replaced. Another even more significant measure of a grinding wheel's utility is the "Quality Measure", ( $S^2/W$ ), which takes into account not only the amount of metal that a wheel can remove, but also the rapidity with which this occurs.

Table 3

Wheel Properties/Performance: Wet grinding 52100 Steel					
Bond Used	Comp.Dens. g/cm <sup>3</sup>	MRR in <sup>3</sup> /min.in	Power HP/in.	G-Rat. S/W	Quality S <sup>2</sup> /W
Glass-cer.	2.262	0.809	14.1	134.5	108.7
		1.348	16.0	162.9	219.7
		2.020	18.6	147.7	298.3
HA4C	2.260	0.757	16.3	118.4	89.7
		1.287	18.9	130.0	167.3
		1.906	21.1	129.8	247.4

\* 1 inch = 2.54 cm

From Table 3 it is apparent that both the G-Ratio and the Quality Measure were markedly improved by the use of the glass-ceramic bond. It may also be observed that the wheel with the glass-ceramic bond cuts faster for a given power output.

As will be appreciated the glass-ceramic bonded products of the invention are extremely versatile and can be tailored to almost any specification. The key variable is the firing schedule which varies with the formulation and the desired density of the crystal structure in the matrix. At all events it is necessary to ensure that the crystallization does not interfere with the flow and wetting of the grains or the formation of dense bond posts. Within these limitations, the crystallization can occur at any convenient time and extent.

The abrasive grain which is bonded by the glass-ceramic is not limited to the seeded sol gel alpha aluminas described above. Indeed any abrasive particles, or mixtures of particles, may be used. These could include for example, fused alumina, silicon carbide, cubic boron nitride, fused alumina/zirconia, diamond or any of the modifications or variations of any of the above, as well as others that are less commonly encountered. With some combinations it may be necessary to add other components to enhance interactions between the grain and the bond. As a rule the presence of these in no way detracts from the usefulness of the products of the invention.

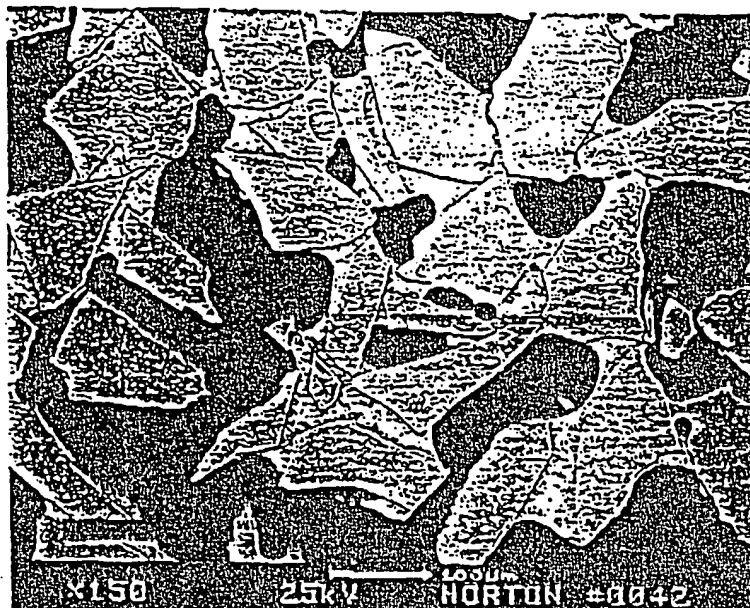
The abrasive products can be made into any useful shape such as a wheel, a hone, a pad, a wheel segment, and the like. It is however noted that the invention has its greatest utility in the application in which the strength of the bond is most tested and this tends to be in the context of grinding wheels.

#### Claims

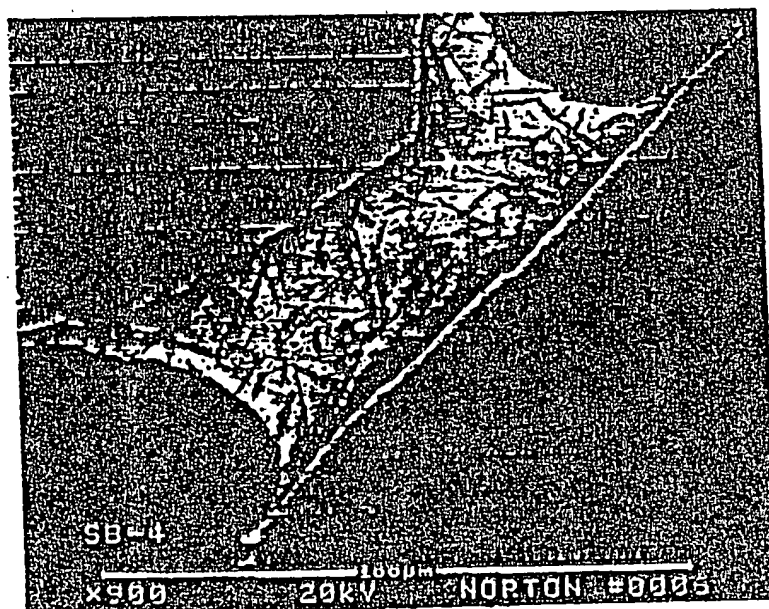
1. An abrasive article that comprises abrasive grains bonded together by a glass-ceramic material wherein preferably at least about 75% of the bond material is located in bond posts or in a coating on the abrasive grains.
2. The abrasive article according to claim 1 in which at least about 85% of the bond material is located in bond posts or in a coating on the abrasive grains.
3. The abrasive article according to claim 1 or 2 in which the glass-ceramic comprises at least 50% by volume of crystalline material.
4. The abrasive article according to claim 3 in which the glass-ceramic comprises at least 80% by volume of crystalline material.
5. The abrasive article according to one of the preceding claims in which the volume proportion of bond to grain is from 0.06 to 0.6.
6. The abrasive article according to claim 5 in which the volume proportion of bond to grain is from 0.1 to

0.4.

7. The abrasive article according to one of the preceding claims in which the abrasive material is an alpha alumina with an average microrcrystalline size of less than one  $\mu\text{m}$ .
8. The abrasive article according to one of the preceding claims in which the bond material is formed from a lithium aluminosilicate frit.
9. The abrsvie article according to one of the preceding claims in which the glass-ceramic and the grain have coefficients of thermal expansion that are within about 20% of each other.
10. The abrasive article of one of the preceding claims which is a grinding tool especially a grinding wheel.

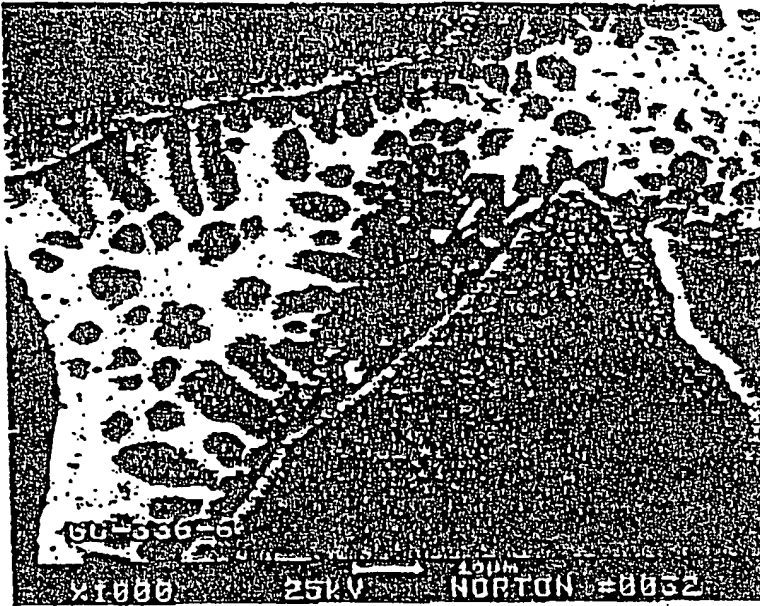


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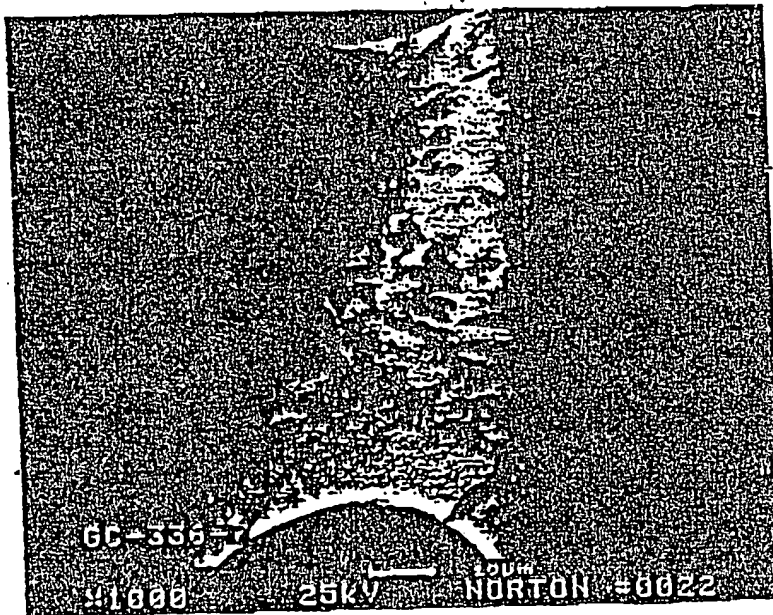


1(b)

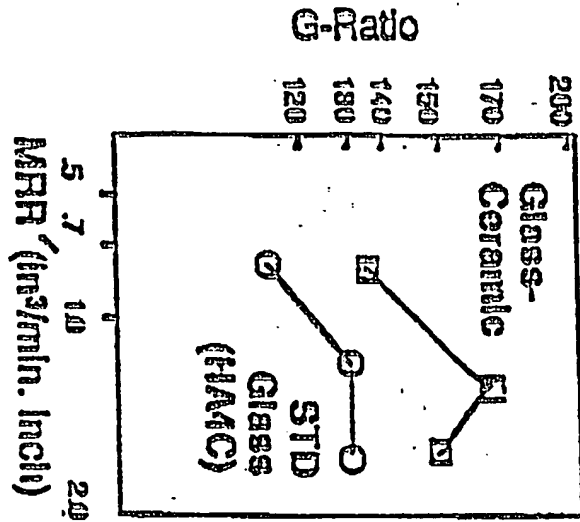




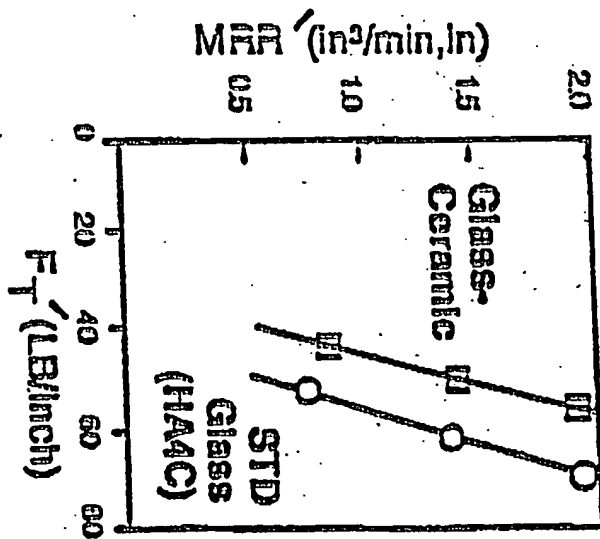
2(a)



2(b)



3 (a)



3 (b)

1 in. = 2.54 cm

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54 Abrasive articles.

57 Abrasive articles especially tools are described which comprise abrasive grits held in a glass-ceramic bond in which at least 75% of the bond material is in bond posts or in coatings on individual grains.

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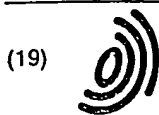
# EUROPEAN SEARCH REPORT

Application Number

EP 92 10 0145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y A	US-A-4 951 427 (PHILIPPE D. ST. PIERRE)  * column 2, line 5 - column 3, line 48 * * claims 1-12, 17-22, 26-30, 39 *	1-6, 10 9	B24D3/14
Y	WO-A-9 001 397 (THE DOW CHEMICAL COMPANY)  * page 3, line 6 - line 23 * * page 6, line 17 - page 7, line 31 * * claims 1-10 *	1-6, 10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B24D C09K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 MAY 1992	Examiner MOLTO PINOL F.J.
<b>CATEGORY OF CITED DOCUMENTS</b>  X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  A : member of the same patent family, corresponding document			

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(54) Lithium aluminoborate glass-ceramics

(57) This invention is directed to the production of thermally crystallizable glasses which, upon heat treatment in contact with alumina particulates, will form a strong glass-ceramic-bonded composite body, the excellent bonding being attributed to the presence of lithium aluminoborate crystals. The glass-ceramic composition consists essentially, in weight percent, of

SiO <sub>2</sub>	25-55	MgO	0-12
B <sub>2</sub> O <sub>3</sub>	35-65	Li <sub>2</sub> O+MgO	4-16
Li <sub>2</sub> O	2-15		

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## Description

This invention is related to the production of glass-ceramic materials having compositions especially well suited for bonding particulate ceramic materials into dense, strong composite articles.

The fabrication of composite articles comprising particulate ceramic materials bonded with a glass-ceramic has been practiced for a number of years. Examples are illustrated in U. S. Patents No. 4,861,734, 5,112,777, and 5,256,603.

The Patent No. 5,112,777 describes a field of divalent metal borate and borosilicate glass compositions that yield unusually strong glass-ceramic bonds when combined with  $Al_2O_3$  and/or other ceramic phases in particulate form and fired. The crystalline phases, consisting principally of borate and/or alumina borates, can develop as a direct result of reaction/dissolution of borate or borosilicate glasses with refractory ceramic phases, most commonly  $Al_2O_3$ .

Our laboratory investigations have discovered a new family of thermally crystallizable lithium borosilicate glasses which can react with particulate  $Al_2O_3$  in a different fashion from that described in Patent No. 5,256,603, supra, to form an exceptionally strong glass-ceramic bond with the particulate  $Al_2O_3$ , as measured in flexural and compression tests performed on fired composite articles. The preferred composite articles are comprised of about 10-30% by weight lithium borosilicate glass powder and about 70-90% by weight of alumina particles. The materials are mixed together, shaped into an article of a desired configuration, and then fired at temperatures between about 750°-950°, preferably 850°-900°C, for a period of time sufficient to cause the particles to react together to form a sintered glass-ceramic-bonded ceramic composite comprising  $Al_2O_3$  particulates bonded together by a glass-ceramic.

The bonding glass-ceramic comprises an interlocking, cross-bladed network of lath-like lithium aluminoborate crystals developed through interaction of the lithium borosilicate glass with the particulate  $Al_2O_3$  during the sintering firing. Because of the very high strengths exhibited by these glass-ceramic bonds, they can provide a significant improvement in the performance of bonded alumina composites for applications such as abrasives, coatings, and electronic substrates. The inventive bonded composites demonstrate properties that can make them competitive in the abrasive field with the much more expensive super abrasives.

The precursor glasses to be fired into the desired glass-ceramic bonds consist essentially, expressed in terms of weight percent on the oxide basis, of about

$SiO_2$	25-55	MgO	0-12
$B_2O_3$	35-65	$Li_2O+MgO$	4-16
$Li_2O$	2-15		

The expression "consist essentially of" is intended to allow the inclusion of minor portions of inorganic oxide components that are not detrimental to the desired properties of the inventive glass-ceramic and, most vitally, do not adversely affect the bond developed through the interaction of the lithium borosilicate glass with the particulate alumina.

The above-cited composition intervals have been found to be critical in producing glasses exhibiting the demanded properties. To illustrate:

At least 25%  $SiO_2$  is required to assure good glass flow and wetting of the alumina particles, and to inhibit essentially instantaneous crystallization when the precursor glass is subjected to the crystallization heat treatment. That is, the glass must flow sufficiently to wet and react with the alumina particles to form the desired bond. The presence of  $SiO_2$  also enhances the chemical durability of the glass. Where the level of  $SiO_2$  exceeds 55%, however, the glass becomes quite refractory and flow thereof is reduced. Furthermore, high levels of  $SiO_2$  can render the glass prone to phase separation.

A concentration of  $B_2O_3$  of at least 35% is required to assure good flow of the glass. That is,  $B_2O_3$  levels less than 35% result in glass exhibiting relatively high refractoriness with consequent less flow. On the other hand, concentrations of  $B_2O_3$  above 65% lead to decreased chemical durability in the glass and unwanted crystallization, e.g.,  $9Al_2O_3 \cdot 2B_2O_3$  crystals may occur.

The presence of at least 2%  $Li_2O$  assures good glass flow and the formation of the lithium aluminoborate crystal phase, that phase believed to have the formula  $2Li_2O \cdot 3Al_2O_3 \cdot 2B_2O_3$ , but its adverse effect upon the overall cost of the bond is one basis for limiting its use to 15%. Furthermore, the reaction of high  $Li_2O$  bonds with  $Al_2O_3$  in combination with  $SiO_2$  can lead to crystal phases other than the desired aluminoborate bond.

Because of their high fluxing action and their adverse effect upon the formation of the desired lithium aluminoborate phase, the preferred inventive materials will be essentially free from the alkali metal oxides  $Na_2O$  and  $K_2O$ . By the expression "essentially free from", it is meant that the glass does not contain an amount of a component, for example,  $Na_2O$  and/or  $K_2O$ , sufficient to alter the chemical and/or physical characteristics of the precursor glass and/or the final glass-ceramic. Preferably, the component will be absent entirely, but that circumstance is not always possible because the batch materials frequently contain the component as an impurity.

MgO appears to augment the action of  $\text{Li}_2\text{O}$ , thereby enabling the level of  $\text{Li}_2\text{O}$  to be maintained at a lower value, while still forming large amounts of the desired crystalline bond phase. It is believed that MgO may form a solid solution within the  $2\text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$  crystal, perhaps  $\text{MgO} \cdot \text{Li}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ . MgO also seems to improve the chemical durability of the glass. Concentrations in excess of 12%, however, hazard the development of unwanted refractory crystal phases, such as spinel, in reacting with the particulate alumina.

Laboratory experimentation has indicated that the most desirable physical characteristics will typically be exhibited, both in the precursor glasses and in the crystallized glass-ceramic, in those glass compositions consisting essentially solely of  $\text{Li}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ , and, optionally, MgO. Nevertheless, minor additions, generally less than a total of 10%, of compatible inorganic metal oxides such as, for example,  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{MnO}$ ,  $\text{PbO}$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{ZrO}_2$ , can be included to modify the properties demonstrated by the glass and those of the glass-ceramic alumina composite body. Care must be exercised in adding extraneous oxides, however, to avoid the generation of low melting glassy, i. e., uncrystallized, phases in the final product.

The method for preparing the inventive composite bodies comprises the five general steps recited below:

- (a) a batch for a thermally crystallizable glass having a composition within the above ranges is melted;
- (b) that melt is cooled to a glass body and that body is comminuted to a finely-divided powder;
- (c) that powder is blended thoroughly with finely-divided alumina to form a homogeneous mixture of the powders;
- (d) that mixture of powders is shaped into a body of a desired configuration; and
- (e) that body is heated to a temperature and for a time sufficient to sinter the glass particles together into an integral body while wetting the particles of alumina to a sufficient extent to react with the alumina particles to thereby develop a strong bond with the alumina powders.

As mentioned above, sintering temperatures as low as  $750^\circ\text{C}$  can be operable with certain glass compositions. It is well-recognized in the art, however, that sintering, crystallization, and matrix filling reactions take place more rapidly as the temperature is raised. Furthermore, it is also well-recognized in the art that the time necessary for sintering, crystallization, etc., is dependent upon the temperature at which the reactions are carried out. Finally, it is well-recognized in the art that very high reaction temperatures can lead to thermal deformation of the body, extensive reactions that can produce undesirable phases, and even to volatilization of the glass components. Accordingly, a temperature of about  $950^\circ\text{C}$  has been deemed to comprise a judicious maximum heat treating temperature. Periods of time ranging about 2-24 hours can be utilized. In general, to assure essentially complete reaction with the alumina particles, a firing period of about eight hours has been deemed to be a practical compromise.

Whereas the three United States patents discussed above, viz., Patent No. 4,861,734, Patent No. 5,112,777, and Patent No. 5,256,603, are believed to constitute the most pertinent prior art, the two patents briefly reviewed below are distantly related to the subject invention.

United States Patent No. 3,006,775 (Chen) discloses and claims the production of glass-ceramic articles consisting essentially, in weight percent, of

$\text{Li}_2\text{O}$	4-30	$\text{Al}_2\text{O}_3$	3-25
$\text{SiO}_2$	50-80	Fluxing Agent	0-15

wherein  $\text{B}_2\text{O}_3$  is recited as being a potential fluxing agent. The resulting glass-ceramics contain lithium aluminum silicate crystals and/or lithium silicate crystals, and the use of the materials as a bonding agent for alumina is noted. Nevertheless, it is immediately evident that the level of  $\text{B}_2\text{O}_3$  is far below the minimum 25% mandated by the Applicants and the crystal phases are unlike those of the Applicants.

United States Patent No. 5,024,974 (Nakamura et al.) discloses and claims glasses exhibiting nonlinear optical effects through the presence of ultrafine particles of  $\text{CuCl}$  and/or  $\text{CuBr}$  particles contained therein. The base glasses consist essentially, in mole percent, of

$\text{SiO}_2$	10-70	$\text{LiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O}$	0.1-50
$\text{B}_2\text{O}_3$	30-90	$\text{CuCl} + \text{CuBr}$	0.01-10
$\text{Al}_2\text{O}_3$	0.01-40		

There is no reference to particulate alumina or to the operability of the glass compositions to form bonds with those particles. There is no mention of aluminoborate crystals; the sole crystals described consisted of  $\text{CuCl}$  and/or  $\text{CuBr}$ .

Table I reports a number of glass forming compositions, expressed in terms of parts by weight on the oxide basis, illustrating the subject invention. Because the sum of the components totals or very closely approximates 100, for all practical purposes, the tabulated values may be considered to represent weight percent. The actual batch ingredients

can comprise any materials, either the oxides or other compounds, which, when melted together, will be converted into the desired oxide in the proper proportions. For example,  $\text{Li}_2\text{CO}_3$  and  $\text{MgCO}_3$  can constitute the sources of  $\text{Li}_2\text{O}$  and  $\text{MgO}$ , respectively.

The batch materials were compounded, thoroughly blended together to assist in obtaining a homogeneous melt, and charged into platinum crucibles. The crucibles were then introduced into a furnace operating at a temperature of about  $1500^\circ\text{C}$  and maintained therewithin for about 1-2 hours.

To reduce the time and energy necessary to comminute the glass to finely-divided particles, the melts were often poured as a fine stream into a bath of tap water. This procedure, termed "drigaging" in the glass art, breaks up the stream of molten glass into small fragments which can then be milled or otherwise powdered to the desired particle size. Another technique commonly used to achieve the same goal includes running a stream of molten glass between metal rollers to form a thin ribbon of glass which was thereafter crushed and milled to the desired particle size.

It must be appreciated that the above description of mixing, melting, and forming procedures reflects laboratory activity only. The inventive glass compositions are capable of being processed utilizing mixing, melting, and forming practices conventionally used in commercial glassmaking. Thus, it is only required that the batch constituents be thoroughly blended together, melted at a sufficiently high temperature for an adequate period of time to secure a homogeneous melt, and subsequently shaped into a glass body.

The glass was reduced to powders having an average particle diameter of about  $10\mu\text{m}$  through ballmilling using  $\text{Al}_2\text{O}_3$  cylinders as the milling media and methanol as the milling aid. After drying, the powders were thoroughly mixed with  $\text{Al}_2\text{O}_3$  powders passing a No. 80 U. S. Standard Sieve ( $117\mu\text{m}$ ) in a vibratory mixer.

TABLE I

	1	2	3	4	5	6
$\text{Si}_2\text{O}$	26.2	41.5	38.8	37.0	47.2	51.5
$\text{B}_2\text{O}_3$	60.7	48.1	48.3	53.7	41.0	39.9
$\text{Li}_2\text{O}$	13.1	10.4	12.9	9.3	11.8	8.6
	7	8	9	10	11	12
$\text{Si}_2\text{O}$	46.6	45.5	51.2	50.8	34.4	52.3
$\text{B}_2\text{O}_3$	43.3	42.3	39.6	39.3	53.2	40.4
$\text{Li}_2\text{O}$	7.0	6.8	6.4	4.2	8.6	4.4
$\text{MgO}$	3.1	--	2.9	5.7	3.9	2.9
$\text{MnO}$	--	5.4	--	--	--	--
	13	14	15	16	17	18
$\text{SiO}_2$	48.4	48.7	46.2	44.0	44.3	42.3
$\text{B}_2\text{O}_3$	37.4	37.7	44.7	42.5	42.8	40.1
$\text{Li}_2\text{O}$	6.1	8.1	3.9	3.7	5.5	6.5
$\text{MgO}$	8.1	5.5	5.2	9.8	7.4	2.9
$\text{Al}_2\text{O}_3$	--	--	--	--	--	7.3
	19	20	21	22	23	24
$\text{SiO}_2$	43.7	44.5	48.4	40.8	43.5	43.2
$\text{B}_2\text{O}_3$	33.8	43.0	37.4	47.3	42.0	41.7
$\text{Li}_2\text{O}$	5.5	5.6	4.0	5.1	7.2	5.4

Continuation of the Table on the next page



TABLE I (continued)

	1	2	3	4	5	6
	7	8	9	10	11	12
	13	14	15	16	17	18
	19	20	21	22	23	24
MgO	4.9	5.0	5.4	6.8	7.3	9.7
ZnO	--	2.0	--	--	--	--
MnO	--	--	4.8	--	--	--

In order to evaluate porous samples for potential use in bonded abrasives, small (3.5 grams) composite pellets were formed by mixing glass frit [particles passing a No. 325 U.S. Standard Sieve (44  $\mu\text{m}$ )], ceramic particles passing a No. 80 U.S. Standard Sieve (177  $\mu\text{m}$ ), and small amounts of water at concentrations calculated to yield specific grain-bond proportions. The mixtures were blended by hand, after which cylindrical pellets were dry pressed at 10,000 psi ( $\sim 703 \text{ kg/cm}^2$ ) and fired according to selected heat treating schedules. For strength measurements, at least three pellets were prepared and tested at each conditions and the measurements averaged.

After visual examination, the fired composite pellets were subjected to axial compression strength measurements, those values providing a measure of crushing strength. Where compositions and firing schedules yielded particularly high compression strengths, discs thereof having a diameter of 1.5" ( $\sim 3.8 \text{ cm}$ ) and weighing 18 grams were prepared and fired in a manner similar to the pellets fired above. Those discs were submitted for modulus of rupture (MOR) testing utilizing a standard piston-on-three-ball technique.

Table II reports the heat treatment schedules applied to the 3.5 gram composite pellets and the 18 gram discs employing an electrically heated furnace. After the final hold temperature, the pellets were cooled at furnace rate; i.e., the electric current to the furnace was cut off and the pellets were allowed to cool to room temperature retained within the furnace.

Table II recites the dwell temperature in  $^{\circ}\text{C}$ , along with a qualitative appraisal of the bond crystallinity as estimated via x-ray diffraction analysis of fine powders, a measurement of flexural strength reported as modulus of rupture (MOR), and a measurement of compressive strength, both of those measurements being expressed in terms of MPa and Ksi (thousand psi).

TABLE II

Example	Heat Treatment	Bond Crystallinity	MOR	Compression
1	800	Very High	60.72 MPa; 8.8 Ksi	234.6 MPa; 34 Ksi
2	900	High	70.38 MPa; 10.2 Ksi	255.3 MPa; 37 Ksi
3	850	Very High	--	255.3 MPa; 37 Ksi
4	850	High	--	248.4 MPa; 36 Ksi
5	900	Medium	71.07 MPa; 10.3 Ksi	227.7 MPa; 33 Ksi
6	850	Low	84.87 MPa; 12.3 Ksi	255.3 MPa; 37 Ksi
7	900	High	85.56 MPa; 12.4 Ksi	255.3 MPa; 37 Ksi
8	825	Low	86.25 MPa; 12.5 Ksi	282.9 MPa; 41 Ksi
9	900	Medium	85.56 MPa; 12.4 Ksi	269.1 MPa; 39 Ksi
10	850	High	80.04 MPa; 11.6 Ksi	289.8 MPa; 42 Ksi
11	850	High	--	262.2 MPa; 38 Ksi
12	850	Medium	79.35 MPa; 11.5 Ksi	276.0 MPa; 40 Ksi
13	900	Medium	84.18 MPa; 12.2 Ksi	269.1 MPa; 39 Ksi
14	900	High	80.04 MPa; 11.6 Ksi	269.1 MPa; 39 Ksi

Continuation of the Table on the next page

TABLE II (continued)

Example	Heat Treatment	Bond Crystallinity	MOR	Compression
15	900	Medium	82.80 MPa; 12.0 Ksi	269.1 MPa; 39 Ksi
16	900	Medium	87.63 MPa; 12.7 Ksi	269.1 MPa; 39 Ksi
17	900	Medium	91.08 MPa; 13.2 Ksi	262.2 MPa; 38 Ksi
18	900	Medium	74.52 MPa; 10.8 Ksi	262.2 MPa; 38 Ksi
19	900	Medium	91.08 MPa; 13.2 Ksi	310.5 MPa; 45 Ksi
20	900	Medium	91.77 MPa; 13.3 Ksi	248.4 MPa; 36 Ksi
21	900	Medium	93.15 MPa; 13.5 Ksi	269.1 MPa; 39 Ksi
22	900	Medium	92.46 MPa; 13.4 Ksi	282.9 MPa; 41 Ksi
23	900	Medium	96.60 MPa; 14.0 Ksi	269.1 MPa; 39 Ksi
24	900	Medium	103.5 MPa; 15.0 Ksi	241.5 MPa; 35 Ksi

The very high mechanical strengths demonstrated by the sintered glass-ceramic-bonded  $Al_2O_3$  particles strongly recommend the inventive thermally crystallizable glasses as bonding media for particulate  $Al_2O_3$  in such applications as grinding wheels and other abrasive products where  $Al_2O_3$  particles comprise the abrasive material.

Whereas the above laboratory work was drawn to forming bulk bodies, it will be appreciated that the inventive materials can be applied as coatings on high temperature refractory ceramics and metals, and as substrates for microelectronic circuitry.

Founded in an overall matrix of physical properties, the glass-ceramic-bonded  $Al_2O_3$  composite comprising Example 17 sintered at 900°C has been deemed to comprise the most preferred embodiment of the invention.

#### Claims

1. A thermally crystallizable glass consisting essentially, expressed in terms of weight percent on the oxide basis, of

$SiO_2$	25-55	$MgO$	0-12
$B_2O_3$	35-65	$Li_2O+MgO$	4-16
$Li_2O$	2-15		

2. A thermally crystallizable glass according to claim 1 also containing up to 10% total of at least one inorganic metal oxide selected from the group consisting of  $Al_2O_3$ ,  $CeO_2$ ,  $La_2O_3$ ,  $MnO$ ,  $PbO$ ,  $TiO_2$ ,  $ZnO$ , and  $ZrO_2$ .
3. A thermally crystallizable glass according to claim 1 having a composition which is essentially free from  $Na_2O$  and  $K_2O$ .
4. A sintered glass-ceramic-bonded ceramic composite body comprising about 70-90% by weight of alumina particulates and about 10-30% by weight of glass-ceramic, said glass-ceramic being crystallized in situ from a glass consisting essentially, expressed in terms of weight percent on the oxide basis, of

$SiO_2$	25-55	$MgO$	0-12
$B_2O_3$	35-65	$Li_2O+MgO$	4-16
$Li_2O$	2-15		

5. A composite body according to claim 4 wherein said glass-ceramic is bonded to said alumina particulates through lithium aluminoborate crystals.
6. A composite body according to claim 4 wherein said thermally crystallizable glass also contains up to 10% total of at least one inorganic metal oxide selected from the group consisting of  $Al_2O_3$ ,  $CeO_2$ ,  $La_2O_3$ ,  $MnO$ ,  $PbO$ ,  $TiO_2$ ,  $ZnO$ , and  $ZrO_2$ .

7. A composite body according to claim 4 wherein said thermally crystallizable glass has a composition which is essentially free from  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

8. A method for forming a sintered glass-ceramic-bonded ceramic composite body comprising about 70-90% by weight of alumina particulates and about 10-30% by weight of glass-ceramic comprising the steps of

(a) melting a batch for a glass consisting essentially, expressed in terms of weight percent on the oxide basis, of

$\text{SiO}_2$	25-55	$\text{MgO}$	0-12
$\text{B}_2\text{O}_3$	35-65	$\text{Li}_2\text{O}+\text{MgO}$	4-16 ;
$\text{Li}_2\text{O}$	2-15		

(b) cooling said melt and simultaneously shaping said melt into a glass body of a desired configuration;

(c) comminuting said glass body into finely-divided powder;

(d) mixing that powder with finely-divided alumina particulates;

(e) shaping said mixture into a body of a desired configuration; and then

(f) heating said body to a temperature and for a period of time sufficient to sinter said glass particles into an integral body while wetting said alumina particulates to a sufficient extent to react with said alumina particulates to thereby develop a strong bond of lithium aluminoborate with said alumina particulates.

9. A method according to claim 8 wherein said glass also contains up to 10% total of at least one inorganic metal oxide selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{PbO}$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{ZrO}_2$ .

10. A method according to claim 9 wherein said glass is essentially free from  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

11. A method according to claim 8 wherein said body is heated to a temperature between about  $750^\circ\text{C}$ - $950^\circ\text{C}$ .

12. A method according to claim 11 wherein said body is heated to a temperature between about  $850^\circ\text{C}$ - $900^\circ\text{C}$ .

13. A method according to claim 8 wherein said body is heated for a period of time ranging about 2-24 hours.



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE-A-21 23 251 (HPC PRODUITS CHIMIQUES S.A.) 30 November 1972 * page 2 - page 4, paragraph 1 *	1-3	C03C10/02 C03C14/00
A	EP-A-0 219 807 (NARUMI CHINA CORPORATION) 29 April 1987 * page 3 * * page 6, line 18 - page 8, line 9 *	1-13	
D,A	US-A-5 256 603 (ANDRUS) 26 October 1993 * column 1, line 48 - column 3, line 23 *	1-13	
D,A	US-A-5 112 777 (MACDOWELL) 12 May 1992 * column 2, line 6 - column 3, line 10 *	1-13	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C03C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>16 January 1996</b>	Examiner <b>Van Bommel, L</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

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(57) 【要約】

【目的】 高密度且つ高強度のスピンルセラミックを提供すること及び簡易な製造法で提供すること

【構成】 スピンル粉末に希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上を添加混合し、焼成し緻密化することを特徴とするスピンルセラミックスの製造方法。

【特許請求の範囲】

【請求項1】 スピンル $MgAl_2O_4$ を主成分とし、希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上を含むスピンルセラミックス。

【請求項2】 希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上の含有量が0.1～30重量%である請求項1記載のスピンルセラミックス。

【請求項3】 スピンル粉末に希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上を添加混合し、焼成し緻密化することを特徴とするスピンルセラミックスの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明スピンルセラミックスは、耐食性を有する高温構造用材料、透光性材料として高温で使用する窓材料等に好適に利用できる。さらにこのスピンルセラミックスは耐放射線性に優れることから、原子力設備の構造材料、機能材料にも利用できる。

【0002】

【従来技術】 スピンルセラミックス ( $MgAl_2O_4$ ) は高い融点をもち、科学的にも安定であるため、耐食性を有する高温構造材料として期待され、また光学的な等

(72) [Inventor]

[Name] Shimamori molten

(57) [Abstract]

[Objective] It offers with thing and simple production method which offer spinel ceramic of the high density and high strength thing

[Constitution] Manufacturing method of spinel ceramic which designates that adding and mixing it does the inside one kind or more of composite oxide of rare earth oxide and rare earth element and other metal element in spinel powder, calcines and densification it does as feature.

[Claim(s)]

[Claim1] Spinel ceramic which designates spinel  $MgAl_2O_4$  as main component, includes inside one kind or more of composite oxide of rare earth oxide and rare earth element and other metal element.

[Claim2] Spinel ceramic which is stated in Claim 1 where content of inside one kind or more of composite oxide of rare earth oxide and rare earth element and other metal element is the 0.1 to 30 weight%.

[Claim3] Manufacturing method of spinel ceramic which designates that adding and mixing it does the inside one kind or more of composite oxide of rare earth oxide and rare earth element and other metal element in spinel powder, calcines and densification it does as feature.

[Description of the Invention]

[0001]

[Field of Industrial Application] Window material charge etc which is used with high temperature it can utilize the this invention spinel ceramic, ideally in high temperature structural material which possesses corrosion resistance and as the translucent material. Furthermore from fact that it is superior in radiation resistance, structural material of nuclear power facility, it can utilize this spinel ceramic even in functional material.

[0002]

[Prior Art] Spinel ceramic ( $MgAl_2O_4$ ) because it is a stability even in scientific with high melting point, was expected, as high temperature structural material which possesses corrosion

方体であるため、透光性材料としての応用も期待されてきた。スピネルセラミックスの製造方法に関する従来技術としては、

(1)  $\text{CaO}$  を添加し、真空及び  $\text{Ar}$  雰囲気中で、 $1500 \sim 1600^\circ\text{C}$  で 1 時間、 $1700^\circ\text{C} \sim 1850^\circ\text{C}$  で 8 時間というような多段階で焼成し緻密にする方法 (R. J. Bratton, J. Am. Ceram. Soc., 57, 283-285 (1974))。

(2)  $\text{Al}_2\text{O}_3$  の材料を用い、ホットプレスにより焼成することで緻密で強度の高いスピネルセラミックスを得る方法 (神崎修三他、窯業協会誌、87, [5], (1979))。

(3) スピネル粉末に比表面積が  $50 \sim 400 \text{ m}^2/\text{g}$  のデルタアルミナ微粉末を加え、焼成し、密度 95% 以上のスピネル焼結体を得る方法 (特開昭 1-296956) がある。

[0003]

[発明が解決しようとする課題] スピネルセラミックスを構造材料として用いる場合緻密で高強度な材料を得ることが必要であるがこれが困難であった。。上記 (1) では、焼結のための雰囲気や温度の厳密なコントロールが必要であり、また (2) ではホットプレス法を用いなければならないため複雑な形状の部品を得ることが難しい。また (3) では、微粉末であるため、取り扱いが容易ではない。本発明は、高密度且つ高強度のスピネルセラミックを提供すること及び簡易な製造法で提供することを目的とする。

[0004]

[課題を解決するための手段] その第一の手段は、スピネル  $\text{MgAl}_2\text{O}_4$  を主成分とし、希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上を含むスピネルセラミックスにある。その第二の手段は、スピネル粉末に希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上を添加混合し、焼成し緻密化することとを特徴とするスピネルセラミックスの製造方法にある。

[0005]

[作用]

(1) 緻密化の促進

希土類の酸化物粉末を添加したスピネル粉末は、添加しない粉末よりも焼結性がよく、同じ条件で焼成した場合より緻密なスピネルセラミックスを得ることができる。

resistance in addition because it is a optical isotropic shape, also application as translucent material was expected. As Prior Art regarding manufacturing method of spinel ceramic,

(1) Method (R.J. Bratton, Journal of the American Ceramic Society (0002-7820, JACTAW) 57, 283-285 (1974)) where it adds  $\text{CaO}$  in vacuum and  $\text{Ar}$  atmosphere, it calcines with kind of multiple steps with  $1500$  to  $1600^\circ\text{C}$  8-hour with 1 hour and  $1700^\circ\text{C}$  to  $1850^\circ\text{C}$  and makes dense.

(2) Method which obtains spinel ceramic where by fact that it calcines making use of material of  $\text{Al}_2\text{O}_3$ , with hot press strength is high with dense (Kanzaki Shuzo other things, refractory industry society magazine, 87, [5], (1979)).

(3) There is a method (Japan Unexamined Patent Publication Showa 1-296956) which specific surface area it calcines in spinel powder including the delta alumina fine powder of  $50$  to  $400 \text{ m}^2/\text{g}$ , obtains spinel sinter of density 95% or higher.

[0003]

[Problems to be Solved by the Invention] When spinel ceramic it uses as structural material, it is necessary to obtain the highly strong material with dense, but this was difficult. With above-mentioned (1), atmosphere for sintering and precise control of temperature are necessary, in addition with (2) hot press method must be used, because, it is difficult to obtain part of complex form. In addition with (3), because it is a fine powder, handling is not easy. this invention designates that spinel ceramic of high density and high strength is offered and that it offers with simple production method as objective.

[0004]

[Means to Solve the Problems] There is a spinel ceramic where means of first designates spinel  $\text{MgAl}_2\text{O}_4$  as the main component, includes inside one kind or more of composite oxide of rare earth oxide and rare earth element and other metal element. Inside one kind or more of composite oxide of rare earth oxide and rare earth element and other metal element adding and mixing it does second means, in spinel powder, calcines and there is a manufacturing method of spinel ceramic which designates that densification it does as feature.

[0005]

[Work or Operations of the Invention]

(1) Promotion of densification

Dense spinel ceramic can be acquired from when as for spinel powder which adds the oxide powder of rare earth, sintering behavior is good in comparison with powder which is not added,

焼結性が良くなる原因の詳細は不明であるが、添加した希土類の酸化物粉末は焼成中、その一部あるいは全部がスピネル粉末と反応することから、何らかのメカニズムにより緻密化に寄与すると考えられる。

#### 【0006】(2) 高強度化

希土類の酸化物粉末を添加し焼成したスピネルセラミックスは、添加しないセラミックスよりも高強度でかつ強度のバラツキの少ないものになる。酸化物粉末が高強度化に及ぼす作用は次の3つが考えられる。

緻密化が促進されることにより、セラミックス内部の気孔が少なくなり、これを起点とした破壊が起こらなくなるため、高強度になる。

添加した酸化物あるいは反応により生じた化合物は焼成中、スピネル粒子の粒成長の障害となる。従って得られるセラミックスの組織は、粒子径が細かく、かつ粗大な粒子を含まず粒子径の比較的小さいものとなる。このため高強度になる。

酸化物粉末粒子あるいは反応により生じた化合物は、焼成後スピネルセラミックス中で均一に分散された状態となる。これが破壊の際のクラック進展の妨げとなり強度が向上する。

添加量は、0.1～30wt%が良い。0.1wt%未満では、焼結性や強度の工場に効果がなく、30wt%より多いと希土類の酸化物そのものの焼結性が良くないため、かえって密度が低下する。

#### 【0007】

【実施例及び比較例】比表面積  $10 \text{ m}^2/\text{g}$ 、純度99.9%の  $\text{MgAl}_2\text{O}_4$  粉末と表1に示す添加物を出発原料とし、表1に示す焼結方法、焼結温度条件でスピネルセラミックスを作製した。

calcines with same condition. Details of cause where sintering behavior becomes good are unclear, but the oxide powder of rare earth which is added while calcining, is thought that it contributes to densification, from fact that one part or all reacts with the spinel powder, with a some mechanism.

#### [0006] (2) High strengthening

Oxide powder of rare earth is added and spinel ceramic which is calcined with the high strength and becomes something where variation of strength is less in comparison with ceramic which is not added. Action which oxide powder causes to high strengthening is thought the following 3.

Air hole of ceramic interior decreases due to fact that densification is promoted, because destruction which designates this as source stops happening, becomes high strength.

Compound which it occurs due to oxide or reaction which it adds while calcining, becomes damage of grain growth of spinel particle. Therefore as for structure of ceramic which is acquired, particle diameter is small, at same time does not include coarse, large particle and becomes the complete set particle diameter relatively. Because of this it becomes high strength.

Compound which it occurs due to oxide powder particle or reaction after calcining becomes state which is dispersed to uniform in spinel ceramic. This case of destruction it becomes interference of crack development and strength improves.

As for addition quantity, 0.1 to 30 wt% is good. When under 0.1 wt%, there is not an effect in factory of sintering behavior and strength, is more than 30 wt% because sintering behavior of oxide itself of rare earth is not good, density decreases rather.

#### [0007]

[Working Example and Comparative Example]  $\text{MgAl}_2\text{O}_4$  powder of specific surface area  $10 \text{ m}^2/\text{g}$  and purity 99.9% and additive which is shown in the Table 1 were designated as starting material, spinel ceramic mix was produced with sintering method and sintering temperature condition which are shown in Table 1.



【表 1】

[Table 1]

試料 No.	添加物 (添加量 (重量%))	焼結方法	焼結温度 (℃)
1	$Y_2O_3$ (0.1)	大気中常圧焼結	1500
2	$Y_2O_3$ (0.1)	大気中常圧焼結	1600
3	$Y_2O_3$ (2)	大気中常圧焼結	1500
4	$Y_2O_3$ (6)	$N_2$ ガス中常圧焼結	1500
5	$Er_2O_3$ (10)	大気中常圧焼結	1500
6	$Y_2O_3$ (25)	ホットプレス	1400
7	$CeO$ (5)	$O_2$ ガス中常圧焼結	1550
8	$Yb_2O_3$ (8)	大気中常圧焼結	1450
9	$Y_2O_3$ (16) + $La_2O_3$ (4)	大気中常圧焼結	1500
10	$Nd_2O_3$ (12) + $Sm_2O_3$ (12)	$Ar$ ガス中常圧焼結	1450
11	$Y_3Al_5O_{12}$ (10)	大気中常圧焼結	1600
12	$Y_2O_3$ (35)	大気中常圧焼結	1500
13	$Y_2O_3$ (33)	$Ar$ ガス中常圧焼結	1600
14	なし	大気中常圧焼結	1500
15	なし	大気中常圧焼結	1750
16	なし	ホットプレス	1500
17	$MgO$ (10)	大気中常圧焼結	1500

注1) ホットプレスは、圧力200 kgf/cm<sup>2</sup>で行った。

注2)  $O_2$  ガス中加圧焼結は、圧力10気圧で行った。

得られたセラミックスの密度、曲げ強度を評価した結果を表2に示す。密度は真密度との比(理論密度比)で示した。曲げ強度は、下スパン30mmの3点曲げ強度測定法で評価した。また、焼結体中の結晶相の存在をX線回折で確認した。

Density of ceramic which it acquires, result of appraising the flexural strength is shown in Table 2. As for density it showed with ratio (theoretical density ratio) of density. You appraised flexural strength, with 3-point bending strength measurement method of lower span 30 mm. In addition, existence of crystal phase in sinter was verified with the X-ray diffraction.

【0008】

[0008]

【表 2】

[Table 2]

No.	理論密度比 (%)	曲げ強度 (kgf/mm <sup>2</sup> )	焼結体中の結晶相
1	95	26	MgAl <sub>2</sub> O <sub>4</sub>
2	99	22	MgAl <sub>2</sub> O <sub>4</sub>
3	99	35	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>
4	99	32	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>
5	97	25	MgAl <sub>2</sub> O <sub>4</sub> . Er <sub>2</sub> O <sub>3</sub> . 未知相
6	95	31	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> . Al <sub>2</sub> O <sub>3</sub>
7	99	32	MgAl <sub>2</sub> O <sub>4</sub> . 未知相
8	99	34	MgAl <sub>2</sub> O <sub>4</sub> . 未知相
9	99	28	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> . 未知相
10	98	26	MgAl <sub>2</sub> O <sub>4</sub> . 未知相
11	97	23	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> .
12	87	18	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> . Al <sub>2</sub> O <sub>3</sub> . Y <sub>2</sub> O <sub>3</sub>
13	89	19	MgAl <sub>2</sub> O <sub>4</sub> . Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> . Al <sub>2</sub> O <sub>3</sub>
14	88	12	MgAl <sub>2</sub> O <sub>4</sub>
15	93	13	MgAl <sub>2</sub> O <sub>4</sub>
16	96	16	MgAl <sub>2</sub> O <sub>4</sub>
17	89	18	MgAl <sub>2</sub> O <sub>4</sub> . MgO

本発明範囲に属するセラミックスNo. 1~13は、曲げ強度が18 kgf/mm<sup>2</sup>以上と高かった。特にNo. 1~11は、いずれも理論密度比が95%以上と高く、また曲げ強度も20 kgf/mm<sup>2</sup>以上と高かった。そして、走査型電子顕微鏡で観察したところ、粗大な粒子を含まず、粒子径の揃ったものとなっていた。また、元素分析したところ、スピネル以外の結晶相が均一に分散していた。

【0009】これに対し、比較例であるNo. 14は添加物なしのため、同条件で焼成した本発明No. 1やNo. 3よりもホットプレス焼結法を用いることで高密度にすることはできたが強度は低かった。また、No. 15とNo. 16は、焼成温度を高くしたり、焼成手段を変えることによって、高密度にすることはできたが強度は低かった。No. 17のセラミックスは希土類酸化物の代わりにMgOを添加したものであるが添加物量を同じくするNo. 5よりも密度、強度ともに低かった。尚、本例では、原料として酸化物粉末を用いたが、これに

As for ceramic No.1 to 13 which belongs to claims of this invention, flexural strength 18 kgf/mm<sup>2</sup> or greater was high.

Especially, as for No.1 to 11, in each case theoretical density ratio 95 % or higher was high, in addition also flexural strength 20 kgf/mm<sup>2</sup> or greater was high. And, when you observe with scanning electron microscope, it did not include coarse, large particle, it had become complete set particle diameter. In addition, when elemental analysis it does, crystal phase other than spinel was dispersed to uniform

[0009] Vis-a-vis this, as for No.14 which is a Comparative Example because of the additive none, it was possible by fact that hot press sintering method is used in comparison with this invention No.1 and No.3 which are calcined with the same condition to make high density but strength was low. In addition, it was possible to make high density, by fact that the No.15 and No.16 make sintering temperature high, change calcining means, but strength was low. ceramic of No.17 is something which adds MgO in place of the rare earth oxide, but both density and strength it was low in comparison with No.5

限らず金属や窒化物等でも良い。

【発明の効果】 高強度、高密度のセラミックスを得ることができる。

which does additive quantity similarly. Furthermore with this example, oxide powder was used as starting material, but it is good even with metal and nitride etc not just this.

[Effects of the Invention] Ceramic of high strength and high density can be acquired.

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APPLICANT : NGK SPARK PLUG CO LTD;

INVENTOR : SHIMAMORI TORU;

INT.CL. : C04B 35/44

TITLE : SPINEL CERAMICS AND ITS PRODUCTION

ABSTRACT : PURPOSE: To obtain high precision and high strength spinel ceramics by adding one or more among oxides of rare earth elements and multiple oxides each of a rare earth element and other metallic element to spinel powder, mixing and firing them and carrying out densification.

CONSTITUTION: Spinel ( $\text{MgAl}_2\text{O}_4$ ) having  $10\text{m}^2/\text{g}$  specific surface area and 99.9% purity is used as a base and one or more among oxides of rare earth elements, e.g.  $\text{Y}_2\text{O}_3$  and multiple oxides each of a rare earth element and other metallic element, e.g.  $\text{Y}_3\text{Al}_5\text{O}_{12}$  are added to the base by 0.1-30wt.%. They are mixed and subjected to pressureless sintering or hot, pressing at 1,400-1,600°C in the air or in gaseous  $\text{O}_2$ ,  $\text{N}_2$  or Ar. The resulting ceramics has  $\geq 95\%$  theoretical density ratio and  $\geq 20\text{kgf/mm}^2$  bending strength.

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(54) 【発明の名称】 スピネルセラミックス及びその製造方法

(57) 【要約】

【目的】 高密度且つ高強度のスピネルセラミックを提供すること及び簡易な製造法で提供すること

【構成】 スピネル粉末に希土類酸化物及び希土類元素と他の金属元素との複合酸化物のうち一種以上を添加混合し、焼成し緻密化することを特徴とするスピネルセラミックスの製造方法。

試料 No.	添加物 (添加量 (重量%))	焼結方法	焼結温度 (℃)
1	Y <sub>2</sub> O <sub>3</sub> (0.1)	大気中常圧焼結	1500
2	Y <sub>2</sub> O <sub>3</sub> (0.1)	大気中常圧焼結	1600
3	Y <sub>2</sub> O <sub>3</sub> (2)	大気中常圧焼結	1500
4	Y <sub>2</sub> O <sub>3</sub> (6)	N <sub>2</sub> ガス中常圧焼結	1500
5	Er <sub>2</sub> O <sub>3</sub> (10)	大気中常圧焼結	1500
6	Y <sub>2</sub> O <sub>3</sub> (25)	ホットプレス	1400
7	CeO (5)	O <sub>2</sub> ガス中常圧焼結	1550
8	Yb <sub>2</sub> O <sub>3</sub> (8)	大気中常圧焼結	1450
9	Y <sub>2</sub> O <sub>3</sub> (16) + La <sub>2</sub> O <sub>3</sub> (4)	大気中常圧焼結	1500
10	Nd <sub>2</sub> O <sub>3</sub> (12) + Sm <sub>2</sub> O <sub>3</sub> (12)	Ar ガス中常圧焼結	1450
11	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> (10)	大気中常圧焼結	1600
12	Y <sub>2</sub> O <sub>3</sub> (35)	大気中常圧焼結	1500
13	Y <sub>2</sub> O <sub>3</sub> (33)	Ar ガス中常圧焼結	1600
14	なし	大気中常圧焼結	1500
15	なし	大気中常圧焼結	1750
16	なし	ホットプレス	1500
17	MgO (10)	大気中常圧焼結	1500

注1) ホットプレスは、圧力200 kgf/cm<sup>2</sup>で行った。

注2) O<sub>2</sub> ガス中加圧焼結は、圧力10気圧で行った。

得られたセラミックスの密度、曲げ強度を評価した結果 回折で確認した。  
を表2に示す。密度は真密度との比 (理論密度比) で示 30 [0008]  
した。曲げ強度は、下スパン30mmの3点曲げ強度測 [表2]  
定法で評価した。また、焼結体中の結晶相の存在をX線